

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

**Joint Institute for the Advancement of
Flight Sciences**

**Program of Research in Severe Storms
NASA Grant NSG 1251**

**(NASA-CR-162764) PROGRAM OF RESEARCH IN
SEVERE STORMS Final Report (George
Washington Univ.) 24 p HC A02/MF A01**

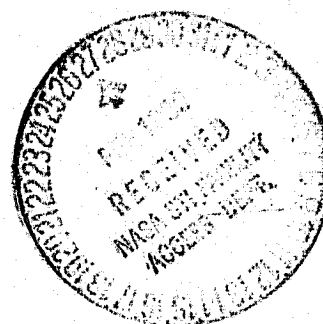
N80-17640

CSCL 04B

G3/47 47166

Unclas

**Final Report
October 31, 1979**



**School of Engineering and Applied Science
The George Washington University
Washington, DC 20052**

I. INTRODUCTION

In recent years, increased attention has been focused on the role of atmospheric chemical species as they relate to public health, climate and weather.¹ Anthropogenic perturbations leading to urban and regional air pollution, stratospheric ozone destruction and resultant climate modifications are of major concern. Much effort has been directed toward the development of predictive models for atmospheric chemistry and transport. In particular, one-dimensional plume and box chemistry models have been developed. Global scale two- and three-dimensional transport models have also received intensive efforts. Currently, some efforts are being made to couple the large scale transport models with simplified chemistry models. Certain areas of the problem remain difficult. The plume and box models are limited to small geographic scales and oversimplified transport assumptions while large scale transport models do not have sufficient resolution to treat point sources and the tropospheric/stratospheric mass exchange that occurs during severe storms.

The research described below is designed to explore two modeling areas, the feasibility of developing a mesoscale chemistry-meteorology interaction model, and the development of a combined urban chemical kinetics-transport model. Work on an additional area of interest, the calculation of some potential energy curves for carbonyl fluoride, CF_2O (which has potential atmospheric interest), was also completed,

II. MESOSCALE MODEL

The goal of this area of research was to examine the feasibility of developing a three-dimensional combined meteorological-chemical kinetics computer program package. The need for such a model was cited in the NASA workshop on Chlorofluoromethanes and the Stratosphere¹ which examined the techniques used and ranges covered by existing atmospheric models. Edinger² has also emphasized the importance of developing a model to adequately describe the chemical dynamics in the atmosphere and the transport of chemical species through the tropopause. Current tropospheric models³⁻⁵ adequately treat the chemical kinetics occurring near the earth's surface; some models also include horizontal transport by using time-averaged wind vectors.³ But, no known model deals with large geographic areas and also includes dynamic meteorology with both horizontal and vertical transport (most focus on one given urban area). Hence, the development of a three-dimensional combined meteorological-chemical kinetics program would provide a unique capability for further understanding atmospheric dynamics.

A suggested starting point for the development of a combined model was a mesoscale meteorological computer program, STORM, written by Michael Kaplan,⁶ which is used to predict severe storm activity. STORM is a three-dimensional hydrostatic real-time model which solves the fundamental Navier-Stokes equations for nonviscous flow. The grid used is comprised of 12 vertical levels with a concentration of levels at the lower altitudes; each vertical level contains 2880 equally-spaced horizontal grid points yielding a total of 34,560 grid points.

A very simple chemical kinetics package containing only nitrogen oxide and ozone reactions would include on the order of 20 chemical species at each grid point. Such an increase of computer storage requirements in the STORM program would exceed the storage capacity of the STAR computer. For this reason, the development of a combined model using the STORM program as a starting point was abandoned in favor of developing a more simplified urban model.

III. URBAN AIR QUALITY SIMULATION MODEL

An urban air quality simulation model was developed in order to predict the temporal and spatial distribution of reactive and nonreactive gases in and around an urban area and to support a remote sensor evaluation program being conducted at NASA Langley Research Center, the Southeastern Virginia Urban Plume Study (SEV-UPS). This model, which is patterned after Schere and Demerjian's⁷ air quality model, treats the urban area as a single cell. The transport and chemistry of the atmospheric species are coupled in order to better simulate the urban area as it was seen by the remote and in situ sensors. The horizontal lengths of the cell are fixed in the beginning of the modeling period, the base of the cell is the ground, and the top of the cell is the mixing layer height which increases during daylight hours. Turbulent uniform mixing is assumed to occur throughout the volume of the cell. All fluxes in the horizontal direction are aligned along the prevailing wind direction through the cell volume. The geographical position of the cell, which is arbitrarily defined by the greatest densities of point and area source emissions, does not change during the simulation period.

even though the wind direction may change; thus, the horizontal fluxes may not always enter the modeling region perpendicular to a horizontal cell face.

The basic working equations governing the prediction of species concentrations are:

$$\begin{aligned} \frac{\partial c_{i,t}}{\partial t} = & \frac{\bar{Q}_i}{z_t} + \frac{\bar{U}}{\Delta x} (c_{i,bg} - c_{i,t-1}) \\ & + \left(\frac{z_t - z_{t-1}}{z_t \Delta t} \right) (c_{i,top} - c_{i,t-1}) + R_i \end{aligned} \quad (1)$$

$$c_{i,t} = \int_{t-1}^t \frac{\partial c_{i,t}}{\partial t} dt \quad (2)$$

where

- $c_{i,t}$ = concentration of species i at time t in ppmv-m⁻³
- \bar{Q}_i = hourly averaged emissions of species i in ppmv-m⁻²
- z_t = height of the mixing layer at time t in m
- $c_{i,bg}$ = concentration of species i at time t-1 upwind of the modeling region in ppmv-m⁻³
- $c_{i,top}$ = concentration of species i above the mixing layer in ppmv-m⁻³
- Δx = horizontal length of the cell in m
- \bar{U} = hourly averaged horizontal wind speed through the cell in m-hr⁻¹
- R_i = differential rate of change of species concentrations due to chemical reactions in ppmv-hr⁻¹

The chemical kinetics describe the interactions of each chemical species with all other species. In general, all $\frac{\partial c_{i,t}}{\partial t}$ are coupled; thus, integration of the equations must be done simultaneously. Various algorithms such as the Gear method⁸ have been developed to perform the integration. Most integration techniques were developed to solve either the kinetic or the transport equations, equations in which the time constants are similar. The combination of transport and kinetics in one equation as in the present model introduces time steps of widely differing magnitudes. This yields a so-called "stiff" set of equations. The Gear method is often inadequate when such stiffness occurs. When the Gear method fails, the EPISODE algorithm,⁹ specially designed to solve stiff equations, can be used. However, the EPISODE package is also limited in the amount of stiffness that can be accommodated but to a lesser degree than the Gear package.

When the stiffness of the differential equations is so great that the EPISODE package fails to provide solutions, approximations to the full differential expressions must be made. Some approximation methods that were used and are described below are not new, having been previously outlined in the Systems Applications, Inc. reports,¹⁰ and are common methods used in chemical kinetics.

The stiffness in the equations can be reduced by separating the chemical species into three groups: 1) those species whose concentration changes are very small relative to their ambient concentrations; 2) those species whose concentrations are of the same order of magnitude as the concentration changes; and, 3) species in which the concentration changes are much larger than the concentrations. The net effect of the separation by groups is to reduce the size of a large matrix from N by N (where N is the number of species) to three smaller matrices and thus make the solution of species

concentrations more reliable. When solving for the concentrations of one group of species, concentrations of species in the remaining two groups are held constant.

Species in group 1, which have low chemical reactivity, have concentration changes that are small relative to their ambient concentrations and include CO_2 , H_2O , N_2 , O_2 , H_2 and the inert gases. The group 2 compounds, those whose diurnal variations in concentration can be measured, include most stable compounds and criteria pollutants such as NO_2 , NO , O_3 , CO , etc. Since the chemical reactions in which the compounds participate are dependent upon concentrations of other species in the group, the rates of change of species concentration in this group, R_i , are coupled to all other species concentrations. Thus the integrations of dc_i/dt for species in this group are performed simultaneously using the EPISODE package.

Species in group 3 are generally compounds with short lifetimes and high chemical reactivity, reaction intermediates; radicals, cations and anions such as OH , $\text{O}(^3\text{P})$, NO_3 and RCO_3 are members of this group. Since the concentrations of the intermediates are at all times much less than the concentrations of reactants and products (group 2 compounds), there is a negligible time lag between the destruction of reactants and the appearance of products. Compared to the concentrations for group 2 compounds, the concentrations for group 3 compounds are negligibly small and effectively zero. Since no group 3 species are directly emitted, the dc_i/dt terms for group 3 species are approximately equal to zero. Simplification of the differential expressions for all species can be accomplished if it is assumed that the dc_i/dt terms for group 3 compounds are exactly equal to zero. Such an assumption is called the steady or stationary state

hypothesis.¹¹ Use of the steady-state assumption does not, however, imply that group 3 compounds are in equilibrium with group 2 compounds. By invoking the steady-state hypothesis, the equations describing the concentrations of group 3 compounds reduce from differential to algebraic nonlinear form. A numerical method that can be used to solve the nonlinear algebraic equations is the Newton-Raphson method.

Meteorology

Hourly averaged meteorological data were measured at stations inside and outside the modeling region. The usable measurements were wind speed, wind direction, temperature, dew point, barometric pressure and solar insolation. A single hourly-averaged value for each parameter was formed using all stations inside the modeling regions and stored for later use in the model.

Averaged values for wind speed and wind direction were used in two ways: to define transport through the cell using equation (1) and to determine which stations upwind of the cell should be used to specify the background concentration $c_{i,bg}$. The dew point measurement was used to select the appropriate vapor pressure of water. Temperature and barometric pressure were used to determine the total number of moles of species in the model; the number of moles was used to maintain conservation of mass and to calculate the concentration of water vapor. Measured solar insolation values were not used, but, in general, only clear days are modeled.

Species Concentrations

Concentrations of O_3 , CH_4 , NO , NO_2 and total hydrocarbons were measured at many stations within and surrounding the modeling region; accuracy limits

on the measurements were set by the experimenters. Averaged concentrations upwind of the cell were calculated using the wind direction to determine upwind stations. The basic procedure for selecting stations was the same regardless of whether the St. Louis RAPS or Tidewater SEV-UPS data set was used. The selection procedure is described below using the RAPS data set for illustration.

An axis system was drawn centered over the modeling region with the 0° of the axis corresponding to the geographic north. Divisions of 45° each were then drawn corresponding to the NE, E, SE, S, etc. directions (see Figure 1). Testing of the wind direction was performed using the divisions as centers of 45° arcs (for example, test if wind direction was between 22.5° and 67.5°). Stations used for determining the background concentrations were selected based on whether the wind direction was located within a given arc. RAPS station locations are shown in Figure 2 while stations used to determine background concentrations as a function of wind direction are listed in Table I. Hourly averaged background concentrations, $c_{i,bg}$ are calculated and stored for later use in equation (1).

Table I

Stations Used to Determine Background Concentration

Wind Direction	Station Numbers
N	114, 115, 116, 120, 121
NE	109, 114, 115, 116, 117
E	109, 114, 115, 116, 117, 118
SE	109, 115, 116, 117, 118
S	109, 117, 118, 119
SW	118, 119, 120
W	118, 119, 120, 121
NW	114, 115, 119, 120, 121

Hourly averaged species concentrations measured at stations within the modeling region were calculated and stored. The measurements for the first hour were used to initialize the model while measurements for other hours were used to compare with calculated concentrations. No distribution of measured total hydrocarbons into reactive hydrocarbon classes was performed.

Anthropogenic emissions (\bar{Q} in equation (1)) were available for the St. Louis RAPS data set and calculated for the SEV-UPS data set as hourly averaged values. The emissions were defined in terms of a somewhat smaller grid than the modeling region; therefore, the smaller grids had to be summed over to obtain the total hourly emissions in the modeling region. In order to account for emissions which might be released above the mixing layer height in the early morning hours as a consequence of a low morning

mixing layer height, a plume rise program was applied to the combined hourly emissions using the measured minimum and maximum mixing layer heights as input. The net effect of the plume rise program was to reduce early morning emissions in some cases.

The emissions classes available in the RAPS data set were nitrogen oxides (NOX), total hydrocarbons (THC), CO, non-reactive hydrocarbons, paraffins, olefins, aromatics and aldehydes. The SEV-UPS emissions inventory, which was compiled specifically for this modeling exercise,¹² was more limited in the emissions available for compilation with only CO, THC and NOX.

Emissions classes were separated into species that were present in the chemical mechanisms. NOX emissions were partitioned into 90% NO and 10% NO₂ while aldehydes were divided into 66% HCHO and 34% other aldehydes. The data was also converted into the uniform units of ppmv.

The entrainment terms, $c_{i,top}$, were obtained from global average concentrations estimated by Heicklen.¹³ A single input value of $c_{i,top}$ for each species was used for all hours of simulation.

Mixing Layer Height

Two options exist for obtaining the hourly mixing layer height, reading measured hourly values into the program, or reading in the bottom and top measured values of the mixing layer height and using a growth curve internal to the program to compute the hourly values. The selection of the proper option is dependent upon the measured hourly values of the temperature gradient. The growth curve is shown in Figure 3 and represents a 74% growth rate between 6 a.m. and 10 a.m., a 16.7% growth rate between

10 a.m. and 12 a.m. and a 9.3% growth rate between 12 a.m. and 3 p.m. No growth occurs later than 3 p.m. when the growth curve is used.

Chemistry

Various chemical mechanisms have been assembled and published that describe the chemical kinetics occurring in the urban troposphere close to the ground. Two recently published mechanisms were used with this model, the Lloyd¹⁴ and Falls and Seinfeld¹⁵ mechanisms. Only portions of the mechanism describing ozone, nitrogen oxide and hydrocarbon kinetics (O_3 - NO_x -HC) were used; no reactions involving sulfur were included. Both mechanisms provide for lumping of hydrocarbon species by reactivity class.

Diurnal variations of photolytic rate constants were computed using an algorithm developed by Schere and Demerjian.¹⁶ Their program computes rate constants for clear sky conditions as a function of actinic flux, date, time and location of the modeled region. No provision was made in this program to reduce the rate constants by an amount proportional to the cloud cover (which reduces radiation intensity incident upon the ground).

The Lloyd mechanism is a composite of mechanisms developed by several workers. The rate constants were updated in the mechanism to reflect the most recently measured data. Hydrocarbons were divided based on bonding characteristics; that is, hydrocarbons were separated into alkanes, alkenes, formaldehyde, other aldehydes, aromatics, cresols, epoxides, organic nitrates, ketones, and various types of organic radicals. Several reactions are net reactions resulting from combining other reactions. Some intermediates that do not appear in the net reaction would have appeared had the reactions not been combined.

A savings in computational time is realized when the number of species can be reduced by combining reactions since computational time for the solution of species concentrations is proportional to the number of species raised to a power (somewhere between 2 and 4). The Lloyd mechanism includes 45 reactions and 37 species and was developed for use in modeling smog chamber data.

The Falls and Seinfeld mechanism has been recently updated by the author to reflect revised rate constant data. While it uses a fewer number of species than the Lloyd mechanism, 30 versus 38, it includes a greater number of chemical reactions, 54. Several photolytic reactions that did not appear in the Lloyd mechanism appear in the Falls and Seinfeld mechanism. Reactions that were combined in the Lloyd mechanism are not combined in this mechanism; several additional reactions have been included. The organic reactants show slightly different product distributions than are used in the Lloyd mechanism; rate constants are also slightly different. The reduced number of species compared with the Lloyd mechanism is a consequence of a different distribution of hydrocarbons into groups: separate groups for aromatics, cresols, epoxides, ketones, and their radicals have been eliminated while organic nitrogen oxides have been more fully separated. Alkanes are not separated by chain length ($\leq C_4$ and $> C_4$) as was done in the Lloyd mechanism.

The dimensions of the current program allow for a maximum of 60 chemical reactions and 45 chemical species with a maximum of eight species per reaction. Estimates of background concentration and entrainment can be input; a single estimate for each parameter is used without change for all hours modeled. Initial species concentrations can also be estimated. Both

photolytic and thermal reactions are treated. Hourly rate constants for photolytic reaction were determined external to the program and input; rate constants and the temperatures at which they were measured were input for thermal reactions. An adjustment in the thermal rate constants that reflects temperature variations is performed every time step.

The concentrations of the coupled species are currently solved by the EPISODE package from the differential rate equations. Subroutines are provided to form the rate equations and the Jacobians of those equations.

The initial concentrations of the steady state species are used as constants in the EPISODE package. Concentrations of the coupled species that are returned from EPISODE are used as constants in the solution of the steady state species concentrations by a modified Newton-Raphson method. Intermediate checks are performed throughout this procedure to determine whether concentrations are approaching zero. The Newton-Raphson method used to solve for the concentrations of steady state species requires external function evaluations for the rates of concentration change and the Jacobians of the functions. The difference between the function evaluations (Equation (1)) for the coupled and steady state species lies in the transport terms for the steady state species. In the absence of chemical reactions for the steady state species, the transport terms are set equal to zero (since $dc_i/dt = 0$ for steady state species). Neglecting transport is further justified if the relatively short chemical lifetimes of steady state species are compared with the long time steps of transport.

Time steps of 0.1 hours are used by the model. In order to limit large concentration fluctuations that would occur if variations in emissions,

background concentrations and meteorological parameters only occurred every hour, linear relationships between adjacent hourly data are formed to interpolate data for time steps for which measured values are not available. Interpolations are performed for photolytic rate constants, emission, mixing layer height and wind speed.

Currently, the method for the solution of concentrations at every time step in the model is being tested. Applications using the RAPS and SEV-UPS data sets will follow the completion of testing.

IV. Potential Energy Curves of Carbonyl Fluoride

Ab Initio projected-unrestricted Hartree-Fock calculations of some potential energy curves of CF_2O were completed during the grant. An abstract for a proposed paper is attached.

V. Publications and Presentations

The following publications and presentations were prepared during the grant support period. Abstracts and reprints may be found in Appendix A.

1. E. E. Remsberg, G. E. Woodbury, L. C. Quinn and D. A. Brewer, "An Emissions Inventory Suitable for Model Studies of Air Quality in Southeastern Virginia," Paper presented at Virginia Academy of Science, May 11, 1979, Richmond, VA.
2. D. A. Brewer, E. E. Remsberg, G. E. Woodbury and L. C. Quinn, "1977 Emissions Inventory for Southeastern Virginia," NASA TM-80119, Sept., 1979.
3. D. A. Brewer and E. E. Remsberg, "Air Quality Model Studies with Applications for Southeastern Virginia," Abstract submitted to AMS/APCA Second Joint Conf. on Applications of Air Pollution Meteorology, March 24-27, 1980, New Orleans, LA.
4. D. A. Brewer, J. C. Schug and D. H. Phillips, "Ab Initio Projected-Unrestricted Hartree-Fock Calculations of Some Potential Energy Curves for Carbonyl Fluoride," Paper to be submitted to J. Chem. Phys.

VI. REFERENCES

1. Robert D. Hudson, editor, "Chlorofluoromethanes and the Stratosphere," NASA RP-1010 (1977).
2. James G. Edinger, "Meteorology at Ground Level," Int. J. Chem. Kinetics Symp. 1, 221 (1975).
3. S. Hameed, R. W. Stewart, S. A. Lebedeff, "A Model Study of the Impact of Emission Control Strategies on Los Angeles Air Quality," Int. Conf. on Envir. Sensing and Assessment, Proc. 1, 1 (1975).
4. T. E. Graedel, L. A. Farrow, and T. A. Weber, "Kinetic Studies of the Photochemistry of the Urban Troposphere," Atm. Envir. 10, 1095 (1976).
5. Steven D. Reynolds, Philip M. Roth and John H. Seinfeld, "Mathematical Modeling of Photochemical Air Pollution - I. Formulation of the Model," Atm. Envir. 7, 1033 (1973).
6. D. A. Paine and M. L. Kaplan, "A Multiscale Numerical Study into the Cascade of Kinetic Energy Leading to Severe Local Storms," Monthly Weather Review, 1977.
7. K. L. Schere and K. L. Demerjian, "A Photochemical Box Model for Urban Air Quality Simulation," Proc., Fourth Joint Conf. on Sensing of Environmental Pollutants, 427-433 (1978).
8. C. W. Gear, "Algorithm 407, DIFSUB for Solution of Ordinary Differential Equations," Comm. A. C. M. 14, 185-190 (1971).
9. A. C. Hindmarsh and G. D. Byrne, "EPISODE: An Effective Package for the Integration of Systems of Ordinary Differential Equations," Lawrence Livermore Laboratory, UCID-30112, Rev. 1, April, 1977.
10. M. K. Liu, D. C. Whitney, J. H. Seinfeld and P. M. Roth, "Continued Research in Mesoscale Air Pollution Simulation Modeling, Vols. I, II, III and IV," EPA Rept. No. EPA-600/4-76-016, May, 1976.
11. S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, 1960.
12. D. A. Brewer, E. E. Remsburg, G. E. Woodbury and L. C. Quinn, "1977 Emissions Inventory for Southeastern Virginia," NASA TM-80119, Sept., 1979.
13. J. Heicklen, "Atmospheric Chemistry," Academic Press, New York, 1976.
14. A. C. Lloyd, "The Role of Computer Modeling of Photochemical Smog in Defining Existing Measurement Needs," NASA RP-1022, pp 255-318, Sept, 1978.

15. A. H. Falls and J. H. Seinfeld, "Continued Development of a Kinetic Mechanism for Photochemical Smog," Envir. Sci. Tech. 12, 1398-1406 (1978).
16. K. L. Schere and K. L. Demerjian, "Calculation of Selected Photolytic Rate Constants over a Diurnal Range," EPA-600/4-77-015, March 1977.

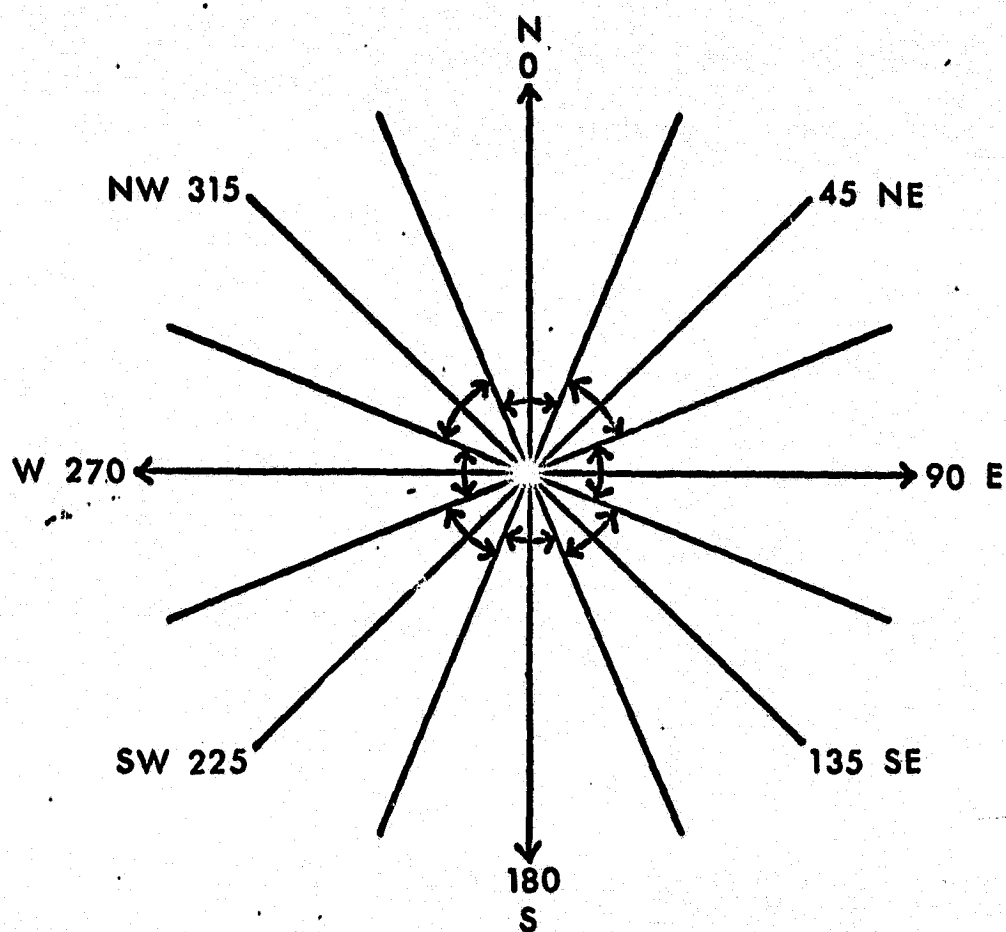


Figure 1.-Arcs of wind direction used to determine background concentration.

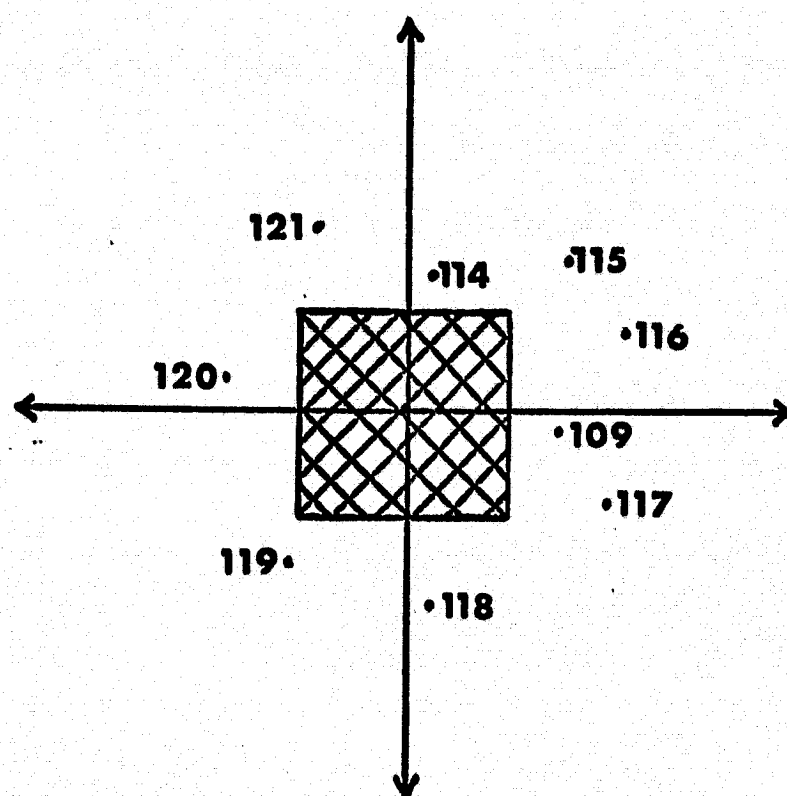


Figure 2.-Geographic locations of RAPS stations used to determine background concentrations.

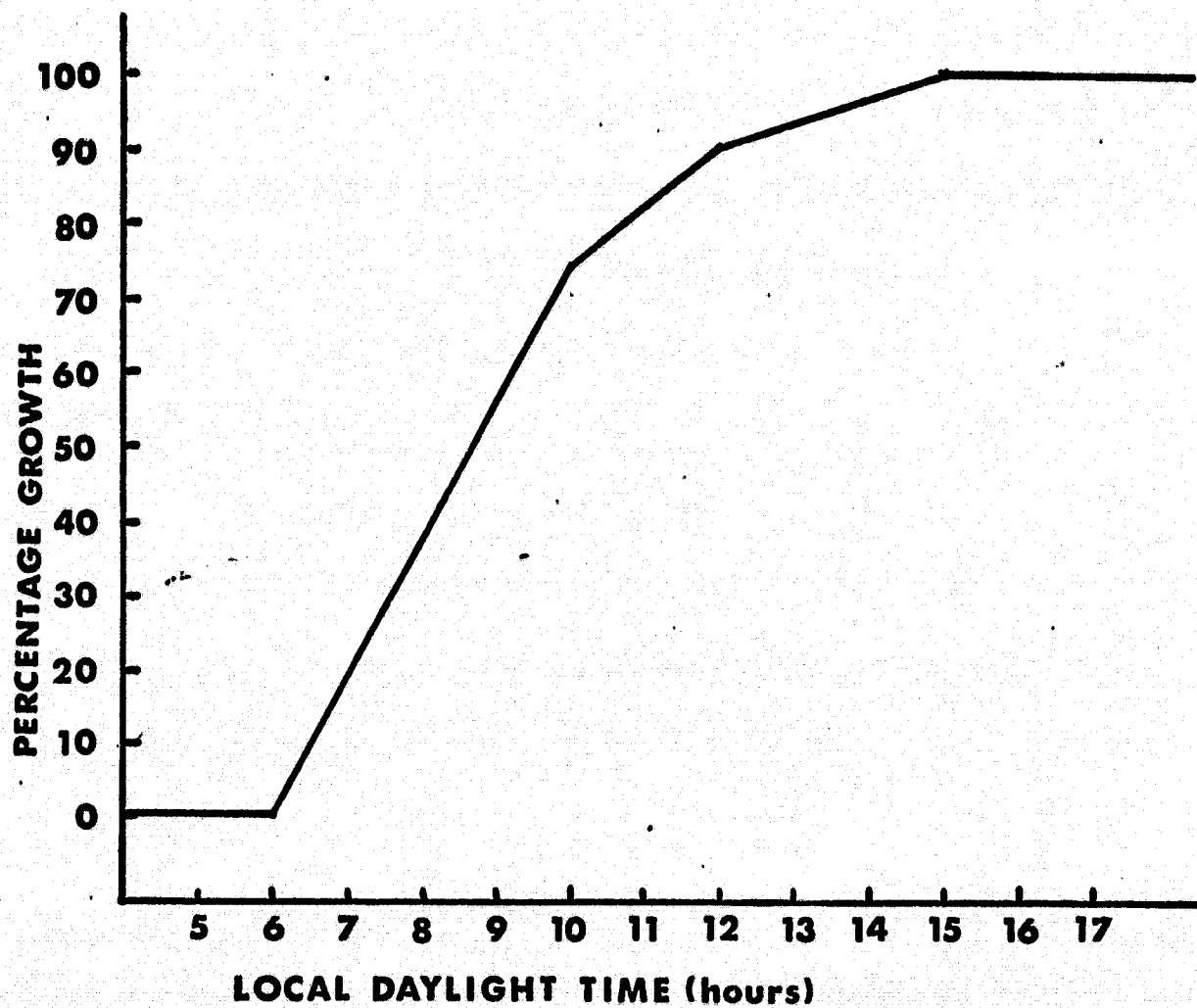


Figure 3.-Growth curve for the mixing layer height.

Appendix A

Abstracts of Publications and Presentations

Paper Presented at Virginia Academy of Science
May 11, 1979, Richmond, VA.

**AN EMISSIONS INVENTORY SUITABLE FOR MODEL STUDIES
OF AIR QUALITY IN SOUTHEASTERN VIRGINIA**

Ellis E. Remsberg, Gerard E. Woodbury, and Linell C. Quinn

**NASA Langley Research Center
Hampton, VA 23665**

and

Dana A. Brewer

**Joint Institute for the Advancement of Flight Sciences
George Washington University
NASA Langley Research Center
Hampton, VA 23665**

One of the largest uncertainties in air quality modeling is in the specification of the source function due to area and point source emissions. Up to now, the area species emissions were available on an annual basis for each city or county in Virginia Region VI. The area compilation from vehicle traffic and other sources that is presented here has been distributed over 1 km^2 grids. The point source data can be superimposed on these grids by using a multiple point source model that includes plume rise information. Consistency checks have been made on the data to assure that the inventory is reasonable. The inventory has been computerized so that it can be more easily updated in the future. These source function data are being applied to a box model calculation of air quality during the summer of 1978, and the results are to be compared with field measurements of ozone and its precursors over that same time period.

Abstract Submitted to AMS/APCA Second Joint Conference on
Applications of Air Pollution Meteorology,
March 24-27, 1980, New Orleans, LA.

**AIR QUALITY MODEL STUDIES WITH APPLICATIONS
FOR SOUTHEASTERN VIRGINIA**

Dana A. Brewer
Joint Institute For Advancement of Flight Sciences
The George Washington University
NASA Langley Research Center
Hampton, Virginia 23665
804-827-3020

Ellis E. Remsberg
NASA Langley Research Center
Hampton, Virginia 23665
804-827-2537

ABSTRACT

An Eulerian urban photochemical air quality simulation model was developed and tested by intercomparing its results with data from selected days of the EPA RAPS air quality inventory. Two separate chemical kinetics schemes (Lloyd (1978) and Falls and Sainfeld (1979)) were considered and calculated species trends were compared with the measured hourly species concentrations of NO_2 , NO , O_3 , and CO . Results of the calculations are sensitive to the initial concentrations of intermediate species. The growth of the morning mixed layer in the model was based on hourly changes in the measured temperature lapse rate in the lowest 25 meters. The success of this parameterization was checked by examining the morning variation of carbon monoxide and nitric oxide, primary pollutants with surface sources. Results of the model validation runs will be presented.

Currently the model is being used to simulate air quality in urban Southeastern Virginia. Preliminary results are available. The authors have compiled an emissions inventory for the region and for several days during the summers of 1978 and 1979 an intensive air quality measurements program was conducted for the area. Vertical profiles of species and temperature have been used to assess the assumption of uniform mixing in the model mixed layer for those days. The urban model has been formulated so that wind fields from a mesoscale model can be applied to the lateral boundaries. With this capability it should be possible to qualitatively determine the role of secondary circulations in a coastal environment on the model air quality results.

**AB INITIO PROJECTED-UNRESTRICTED HARTREE-FOCK CALCULATION
OF SOME POTENTIAL ENERGY CURVES FOR CARBONYL FLUORIDE**

Dana A. Brewer
Joint Institute for the Advancement of Flight Sciences
George Washington University
NASA Langley Research Center
Hampton, Virginia 23665

John C. Schug
Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24060

Donald H. Phillips
NASA Langley Research Center
Hampton, Virginia 23665

ABSTRACT

Some potential energy curves for CF_2O were calculated using Projected-Unrestricted Hartree-Fock (PUHF) theory. All calculations were based on the ground state equilibrium geometry and employed a contracted [4s3p] Gaussian-type atomic orbital basis set. Bound states were found for the X^1A_1 and $1,3A_2$ states while the $1,3B_1$ and $1,3B_2$ states were repulsive in agreement with previous work. The merits of the PUHF treatment compared to Restricted Hartree-Fock and Configuration Interaction calculations are discussed. The vertical spectrum calculated in this work is compared with experimental and previously calculated results. Agreement is good for those transitions involving exclusively valence orbitals. Implications for the atmospheric photochemistry of CF_2O are discussed.